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(54) METHODE POUR L'OBTENTION DE SYSTEMES CATALYTIQUES ORGANOMETALLIQUES STABLES, TRES ACTIFS; FORMULATIONS AINSI OBTENUES

(54) METHOD FOR PRODUCING HIGHLY ACTIVE, STABLE METALLOCENE CATALYST SYSTEMS,AND FORMULATIONS PRODUCED THEREBY

(57) Méthode pour la préparation de formulations stables, homogènes et très actives, constituées essentiellement d'une ou de plusieurs composantes catalytiques organométalliques dans des paraffines; formulations ainsi obtenues.

(57) Disclosed are a method for the production of homogeneous, highly active, stable formulations, consisting essentially of one or more organometallic catalyst components in paraffins, and formulations produced according to this method.

Abstract of the Disclosure

Disclosed are a method for the production of homogeneous, highly active, stable formulations, consisting essentially of one or more organometallic catalyst components in paraffins, and formulations produced according to this method.

METHOD FOR PRODUCING HIGHLY ACTIVE, STABLE METALLOCENE CATALYST SYSTEMS, AND FORMULATIONS PRODUCED THEREBY

Background of the Invention

Metallocene catalyst systems are increasingly gaining in importance as a new generation of catalyst systems for the production of polyolefins ("Single Site Catalysts"). As is already known from classical Ziegler-Natta catalysis, these new catalysts essentially consist of a transition metal compound as a catalyst and a cocatalyst component, for example, an alkylaluminoxane, in particular, methylaluminoxane. Cyclopentadienyl, indenyl, or fluorenyl derivatives of group IVA of the Periodic Table of the Elements are preferably used as the transition metal compound. In contrast to conventional Ziegler-Natta catalysts, such systems have, in addition to a high activity and productivity, not only the capability of a specific control of product characteristics as a function of the components used and the reaction conditions, but, moveover, they open up access to previously unknown polymer structures with very promising characteristics with regard to technical applications.

In the literature, a large number of publications have appeared having as an object the production of special polyolefins with such catalyst systems. What is disadvantageous in almost all cases, however, is the fact that to attain acceptable productivities, a high excess of alkylaluminoxanes, based on the transition metal component, is required (usually, the ratio of aluminum, in the form of

aluminoxane, to transition metal is approximately 1000:1). Due to the high price of the alkylaluminoxanes, on the one hand, and due to the additional polymer work-up steps ("deashing steps"), required in some cases, on the other hand, a polymer production on a technical scale and on the basis of such catalyst systems would frequently be uneconomical. In addition, there is the fact that the solvent toluene, frequently used for the formulation of alkylaluminoxanes, in particular, methylaluminoxane, is increasingly undesired for reasons of the storage stability of highly concentrated formulations (strong tendency to gel formation of the aluminoxane solutions) and for toxicological reasons, with respect to the application range of the polyolefins that result in the long run.

These catalyst systems or their formulations are very sensitive substances that undergo losses in polymerization activity within a few hours or days.

Due to the high price of these modern catalyst systems, such activity losses are not acceptable. For economic reasons, therefore, there has been a need for catalysts or catalyst systems which, after production, remain highly active for a longer period of time or even increase in activity.

According to World Patent No. 93/23439, the stability of metallocene catalyst systems is attained by a comprehensive variation of the preparation conditions, in particular, temperature treatment.

This procedure is expensive, on the one hand, and cannot generally be used because of the sensitivity of the systems, on the other hand.

The goal of the present invention, therefore, is to overcome these disadvantages and to develop homogeneous formulations of metallocene-based catalyst systems that at least retain their high polymerization activity over a long period of time.

Brief Summary of the Invention

Surprisingly, it has been discovered that the polymerization activity of metallocene catalyst systems in the form of paraffin-containing, liquid or solid formulations can be stabilized permanently. The definition formulation, therefore, comprises catalyst systems in high-boiling hydrocarbons (paraffins) of a consistency which is oily or waxy at room temperature, in which the components are dissolved, suspended, or dispersed by means of suitable mixing devices.

An object of the invention is therefore a method for the production of homogeneous mixtures, consisting essentially of at least one metallocene, at least one cocatalyst, and a formulation medium, wherein the preparation of the catalyst component,

A) takes place directly in the formulation medium according to methods which are, in fact, known; or

B) the metallocene-based catalyst components are prepared and isolated separately and then

suspended, dispersed, or dissolved in the formulation medium; or

C) a solution of the metallocene-based catalyst component, produced according to known methods, in a low-boiling solvent, is introduced, in a first step, into the formulation medium, and in a second step, the low-boiling solvent is removed,

D) optionally in the presence of any of the customary inorganic or organic carrier materials, auxiliaries, additives, and/or accessory agents.

Another object of the invention refers to the formulations produced in accordance with the method of the invention.

Other objects of the invention are characterized by the claims.

Detailed Description of the Invention

The formulation media useful according to this invention include all natural or synthetic, commercially available long-chain, optionally branched, liquid or solid hydrocarbons with boiling points above 150°C, preferably above 200°C, and viscosities of at least 1 Pa·sec at 25°C.

These compounds include the product groups of the so-called white mineral oils, e.g. Witco White Mineral Oil Parol® (trademark of Witco Polymers + Resins B.V., Netherlands), petrolatum (Vaseline), and paraffinic waxes, e.g., Terhell® (Schümann Company).

The hydrocarbon used does not depend on the organometallic compound but is determined mainly by practical requirements of future applications.

Compounds of the elements of Groups IIA, IIIA, or IVA of the Periodic Table of the Elements, preferably organoaluminum, organoboron, or organomagnesium substances, alone or in mixtures, or as a complex salt, are used as cocatalysts, in accordance with the invention, such as $R^1R^2R^3Al$, $R^1R^2R^3B$, and R^1R^2Mg, wherein R^1, R^2, R^3 are independently of one another halogen, a heteroatom, or alkyl or alkoxy containing up to 12 carbon atoms, for example: tributylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, diethylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, diisobutylaluminum chloride, isobutylaluminum dichloride, diethylaluminum iodide, diisobutyl hydride, diethylaluminum methoxide, isoprenylaluminum, dimethylaluminum chloride, methylaluminoxane, methylaluminum sesquichloride, tetraisobutyl dialuminoxane, trimethyl aluminum, and/or triethylaluminum, preferably in mixtures with at least one of the compounds diethylaluminum hydride, hexaisobutyltetraluminoxane, diethyl (dimethylethylsilanolato)aluminum, diethyl(ethylmesthylsilanolato)aluminum, diisobutyl(methylsilanolato)aluminum, tridodecylaluminum, tripropylaluminum, dipropylaluminum chloride, dibutylmagnesium, butylethylmagnesium, butyloctylmagnesium,

butyloctylmagnesium ethoxide, ethylaluminum propoxychloride, triethylboron, tris(pentafluorophenyl)borane, and their salts.

As a catalyst component, one can metallocene compounds as described in European Patent Nos. A-0,480,390, A-0,413,326, A-0,530,908, A-0,344,887, A-0,420,436, A-0,416,815, A-0,520,732.

They are, in particular compounds of the following general formula (1):

$$Q(CpRa)(Cp'R'a)M(X)_n \qquad (1)$$

wherein

Cp is a cyclopentadienyl, indenyl or fluorenyl radical;

R and R' are the same or different and each is a C_1-C_{10} alkyl, phosphine, amine, C_1-C_{10} alkyl ether, or C_6-C_{10} aryl ether group with $0 \leq a \leq 4$ and $0 \leq a' \leq 4$;

Cp' is one of the groups Cp or

Cp' is -NR''- wherein R'' is an alkyl or aryl radical and a=1, and

Q is a single bridge or multi bridges

$$\left(R^1-\overset{|}{\underset{|}{Z}}-R^2\right)_b$$

between Cp and Cp', wherein R^1 and R^2 are the same or different and each is a hydrogen atom, C_1-C_{10} alkyl group, or C_6-C_{10} aryl group, and Z denotes carbon, silicon, or germanium, wherein b is 0, 1, 2, or 3,

M is a transition metal of the groups 3 to 6 of the Periodic Table of the Elements (IUPAC notation), in particular Zr or Hf,
X is halogen, in particular, Cl or Br, and
n is the oxidation number of M, reduced by 2.

In particular, the following compounds can be used as bridged ligands, Q(CpRa)(Cp'R'a) in general formula (1):

Dimethylsilylbis(1-indene), dimethylsilylbis(1-cyclopentadiene), 2,2-propylbis(1-indene),
2,2-propylbis(trismethylcyclopentadiene),
2,2-propylbis(5-dimethylamino-1-indene),
2,2-propylbis(6-dipropylamino-1-indene),
2,2-propylbis(4,7-bis(dimethylamino-1-indene)),
2,2-propylbis(5-diphenylphosphino-1-indene),
2,2-propylbis(4,5,6,7-tetrahydro-1-indene),
2,2-propylbis(4-methyl-1-indene), 2,2-propylbis(5-methyl-1-indene),
2,2-propylbis(6-methyl-1-indene),2,2-propylbis(7-methyl-1-indene),
2,2-propylbis(5-methoxy-1-indene),
2,2-propylbis(4,7-dimethoxy-1-indene),
2,2-propylbis(2,3-dimethyl-1-indene),
2,2-propylbis(4,7-dimethyl-1-indene),
2,2-propylbis(1-cyclopentadiene),
2,2-propylbis(1-indene), diphenylmethylbis(1-indene),
diphenylmethylbis(1-cyclopentadiene),
diphenylmethylbis(1-indene),

diphenylsilylbis(1-indene), diphenylsilylbis(1-cyclopentadiene), diphenylsilylbis(1-indene), ethylenebis(1-indene), ethylenebis(trimethylcyclopentadiene), ethylenebis(5-dimethylamino-1-indene), ethylenebis(6-dipropylamino-1-indene), ethylenebis(4,7-bisdimethylamino-1-indene), ethylenebis(5-diphenylphosphino-1-indene), ethylenebis(4,5,6,7-tetrahydro-1-indene), ethylenebis(6-methyl-1-indene), ethylenebis(7-methyl-1-indene), ethylenebis(5-methoxy-1-indene), ethylenebis(4,7-dimethoxy-1-indene), ethylenebis(2,3-dimethyl-1-indene), ethylenebis(4,7-dimethyl-1-indene), ethylenebis(9-fluorene), ethylenebis(1-cyclopentadiene), ethylenebis(1-indene).

As unbridged ligands (formula (1) with b = 0), preferably the following compounds can be used: cyclopentadiene, fluorene, indene, and their monoalkylated or multialkylated derivatives, wherein the alkyl radical can contain 1-10 carbon atoms. In accordance with the invention, the following are preferred: [bis(cyclopentadienyl)]zirconium dichloride, [bis(methylcyclopentadienyl)]zirconium dichloride, [bis(n-propylcyclopentadienyl)]zirconium dichloride, [bis(isobutylcyclopentadienyl)]zirconium dichloride, [bis(cyclopentylcyclopentadienyl)]zirconium dichloride,

[bis(benzylcyclopentadienyl)]zirconium dichloride, [bis(octadecylcyclopentadienyl)]zirconium dichloride, [bis(n-butylcyclopentadienyl)]titanium dichloride, [bis(n-butylcyclopentadienyl)]zirconium dichloride, [bis(n-butylcyclopentadienyl)]hafnium dichloride, [bis(indenyl)]zirconium dichloride, [bis(indenyl)]dimethylzirconium, [bis(tetrahydroindenyl)]zirconium dichloride, [1,2-ethylenebis(indenyl)]zirconium dichloride, [1,2-ethylenebis(indenyl)hafnium dichloride, [1,2-ethylenebis(tetrahydroindenyl)zirconium dichloride, [dimethylsilylbis(1H-inden-1-yl]zirconium dichloride, [dimethylsilylbis(1H-inden-1-yl)]hafnium dichloride.

Porous oxides of one or more of the elements of groups IIA, IIIA, or IVA of the Periodic Table of the Elements, such as ZrO_2, TiO_2, B_2O_3, CaO, ZnO, BaO, preferably aluminosilicates (zeolites), Al_2O_3 and MgO and in particular, SiO_2 (West German Patent No. 4,409,249), are useful as inorganic carrier materials that can be used in accordance with the invention.

Porous, partially polymeric compounds, such as polyethylene, polypropylene, polystyrene, and sugar derivatives (starch, amylose, cyclodextrins), can be taken into consideration as organic carrier materials that can be used in accordance with the invention.

To prepare the formulations of the invention, in accordance with the method of the invention, there are basically different possibilities, for example:

M1) Preparation of the metallocene-based catalyst system in the dispersing /suspending medium or solvent (paraffin), in accordance with the invention.

M2) Dissolution, suspension, or dispersion of already isolated metallocene-based catalyst components in the dispersing medium or solvent (paraffin), in accordance with the invention

M3) Mixing of nonaromatic solvent or dispersing agent with a solution of the metallocene-based catalyst components and subsequent separation of the solvent by means of distillation, thus obtaining the solutions, suspensions, or dispersions, in accordance with the invention.

To prepare the formulations, the catalyst components can be used in pure form as well as on a suitable support material. If the catalyst components are used in pure form, the support material and auxiliaries, additives, and accessory agents can be added to the processing possibilities M1)-M3) at any time.

The following examples illustrate the synthesis of the claimed metallocene-catalyst systems and their testing in the polymerization.

Synthesis Examples

Example 1

Methylaluminoxane in Witco Parol® (trade name of Witco Netherlands)

402 g of a toluene solution of MAO (Al total, 13.2%; Al as TMA, 3.19%) and 219 g Witco Parol® were fed under nitrogen atmosphere to a 1-L flask, equipped with a thermometer and stirrer that moves around the edges. The flask contents were heated in an oil bath to a maximum 32°C and a vacuum was applied. The distilled-off toluene was condensed in a low-temperature trap. It was possible to strengthen the vacuum with the declining toluene content of the suspension. Toluene residues were distilled off at <1 mbar for 3 h.

A viscous and milky-turbid suspension was obtained. The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 13.4%

Al as TMA: 1.5%

Example 2

Methylaluminoxane in Witco Petroleum Jelly Snowwhite MD® (Vaseline, Witco Netherlands)

130.1 g of a toluene solution of MAO (Al total, 13.2; Al as TMA, 3.19%) and 85.1 g White Petroleum Jelly Snowwhite MD® were fed into a 500-mL Schlenk tube, equipped with a stirrer, under a protective nitrogen atmosphere. After heating to 55-60°C in an oil bath, the mixture became homogeneous. The toluene was distilled off in a vacuum and condensed in a low-temperature trap. The vacuum was continuously increased to below 1 mbar, and the bath temperature was maintained at a maximum of 65°C. After complete removal of the toluene, a colorless, homogeneous, waxlike mass was obtained, which flowed at approximately 60°C.

The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 12.0%

Al as TMA: 1.9%

Example 3

Methylaluminoxane in paraffin wax

33.5 g Methylaluminoxane (solid) and 16.8 g paraffin (Terhell 5605®, Schümann Company) were heated under nitrogen in a round-bottomed flask with a stirrer that moves around the edges. With a bath temperature of 65-70°C, a turbid melt was obtained. The melt was allowed to solidify while stirring and then the melt was dissolved from the walls of the

flask. After cooling externally with dry ice, it was possible to comminute the solid to a fine grain solid which could be poured.

The powder, containing approximately 66% MAO, was not pyrophoric or self-igniting.
Al total: 26.1%
Al as TMA: 3.5%

Example 4

Methylaluminoxane in Witco Parol®

26.3 g of a finely pulverized MAO solid (Al total, 39.2%) were stirred with 7.3 g white oil Witco Parol® under a protective argon atmosphere. A colorless, waxlike mass was obtained.

The powder containing approximately 78% MAO was not pyrophoric or self-igniting and exhibited only a moderate gas development upon contact with water. Placed on moist filter paper, carbonization without self-ignition was observed.
Al total: 30.1%
Al as TMA: 3.6%

Example 5

Dispersion of methylaluminoxane in petrolatum (Vaseline)

Under a protective nitrogen atmosphere, 125 g of a toluene solution of MAO (Al total, 13.2%; Al as

TMA, 3.19%) and 78.5 g petrolatum, white, German Pharmacopoeia 10, VARH AB (Schümann Company) were fed into a 500-mL Schlenk tube, equipped with a stirrer. After heating to 55-60°, the toluene was distilled off and condensed in a low-temperature trap. The vacuum was continuously increased to below 1 mbar, and the bath temperature was maintained at a maximum 65°C. After complete removal of the toluene, a colorless, homogeneous dispersion was obtained, which could flow at above approximately 60°C.

The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 12.3%

Al as TMA: 1.6%

Example 6

Suspension of methylaluminoxane and metallocene in white oil

60.5 g of a toluene solution of MAO (Al content, 13.2%; Al as TMA, 3.19%) were fed into a stirring apparatus under a protective argon atmosphere. 2.0 g EURECEN® 5036 (trade name of the Witco Company, Bergkamen, Germany - 1,2-ethylenebis(1-indenyl)zirconium dichloride) were added to this solution, and stirring was carried out for 30 min. 39 g white oil Witco Parol® were metered into this dark-brown solution and heated to 40°C. The toluene was

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distilled off under a vacuum of up to 0.1 mbar and condensed in a low-temperature trap.

56.6 g of a brown, waxlike catalyst mass was obtained.

The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 14.11%

Zr: 0.77%

Example 7

The procedure was carried out as in Example 6. Before use in the polymerization, the mixture was subjected to a 24-h aging process in toluene.

Example 8

The procedure was carried out as in Example 6. Before use in the polymerization, the mixture was subjected to a 48-h aging process in toluene.

Example 9

Suspension of supported MAO/metallocene/silica catalyst system in Witco Parol®

23 g of a supported catalyst system (TA 02954, research product from the Witco Company; Al

content, 23.9%, Zr content 1.1%) were stirred with 53.7 g while oil Witco Parol® in a stirred vessel under a protective argon atmosphere. A dark-brown suspension was obtained.

The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 7.17%

Zr total: 0.33%

Example 10

Metallocene/methylaluminoxane/silica suspension in white oil

203.5 g of a 10% solution of methylaluminoxane in toluene (Al content, 5.0%) were introduced into an apparatus suitable for working under a protective argon atmosphere, with stirrer, thermometer, reflux condenser, and metering of solids.

18.8 g Silica (SYLOPOL 2104®, Grace Company, with 5% water content) were thoroughly shaken with 1.5 g distilled water for approximately 10 min, poured into the solids meter, and slowly added to the stirred methylaluminoxane solution. With gas development (methane gas), the temperature rose to 65°C. After the end of the addition, stirring was carried out until room temperature was once again reached, and then 2.44 g EURECEN® 5036 1,2-ethylenebis(1-indenyl)zirconium dichloride) were added. Stirring

was then carried out for 1.5 h, wherein the flask contents turned red-brown. Then 121.2 g of white oil (Witco Parol®) were added, in order to attain an approximately 25% suspension.

The toluene was completely distilled off at a maximum of 45°C and a vacuum of up to 0.1 mbar in 6 h. A red-brown, highly viscous suspension was obtained.

The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 5.25%

Zr: 0.27%

Example 11

Metallocene/methylaluminoxane/silica suspension in white oil

52.4 g of silica (SYLOPOL® 2104) on which was supported methylaluminoxane, with an aluminum content of 23.8%, was fed under a protective nitrogen atmosphere, and 3.14 g EURECEN® 5036 were added. 111.1 g white oil (Witco Parol®) were added to this mixture of solids and stirred for over 2 h. A viscous, curry-colored 33% suspension was obtained.

The suspension was neither pyrophoric nor self-igniting; slight gas generation took place on addition of water.

Al total: 7.48%

Zr: 0.38%

Comparative examples

In Comparative Examples 12 and 13 a commercial MAO solution, sold by the Witco Company, Bergkamen, Germany, under the trade name EURECEN® Al 5100/10T, was used and together with the other catalyst components, metered directly into the polymerization reactor. The concentrations of the active catalyst material can be seen in Tables I and II.

Polymerization results

Polymerization results and analytical data for homogeneous formulations

Table I*

Example	Formulation	%Al, %Zr in Formulation	Productivity of the formulation, kg PE/mol Zr·h
1	MAO in Parol[1]	13.4; 0.00	30552
2	MAO in Petroleum Jelly[1]	12.0; 0.00	29880
3	MAO (solid) in paraffin	26.1; 0.00	35256
4	MAO in Parol[1]	30.1 0.00	55584
5	MAO in Vaseline (Schümann)[1]	12.3; 0.00	25704
6	MAO/ metallocene[2] prepared in Parol and polymerized immediately	14.11 0.77	3456
7	MAO/ metallocene[2], prepared in Parol and polymerized after 24 h	14.11 0.77	29964
8	MAO/ metallocene[2], prepared in Parol and polymerized after 48 h	14.11 0.77	57288
12	MAO in toluene (Comparative Example)[1]	4.84; 0.00	29328

[1] = Bis(n-butylcyclopentadienyl)zirconium dichloride
[2] = Ethylene-1.2-bis(indenyl) zirconium dichloride

(MAO: 900 g/mol; metallocene, abs. conc. conc. 1.25 x 10^{-6} mol Zr; Al:Zr=1000:1); 900 mL toluene; 30°C inside temperature; 4 bar ethene; 1000 rpm; 20 min)

Polymerization results and analytical data for heterogeneous formulations

Table II

Example	Formulation	%Al	%Zr	Productivity kg PE/mol Zr·h
9	MAO/SiO_2/ Metallocene, suspended in Parol[2)]	7.17	0.33	4200
10	MAO/SiO_2/ Metallocene, prepared in Parol[2)]	5.25	0.27	2228
11	MAO/SiO_2/ Metallocene, prepared in Parol[2)]	7.48	0.38	1081
13	MAO/SiO_2/ Metallocene, suspended in toluene (Comparative Example)[2)]	5.25	0.27	688

[1)] = Bis(n-butylcycolpentadienyl)zirconium dichloride
[2)] = Ethylene-1,2-bis(indenyl)zirconium dichloride

(MAO/SiO_2, 23.8% Al; metallocene abs. conc. 1.25×10^{-6} mole Zr; triisobutylaluminum (Al:Zr=800:1); 900 mL toluene; 40°C inside temperature; 4 bar ethene; 1000 rpm; 20 min)

What is Claimed Is:

1. A method for producing a homogeneous mixture consisting essentially of an optionally supported catalyst system consisting of at least one metallocene and at least one cocatalyst, and a formulation medium, comprising

A) preparing the catalyst system directly in the formulation medium, or

B) preparing separately the catalyst system and then suspending, dispersing or dissolving it in the formulation medium, or

C) introducing a solution of the catalyst system in a low-boiling solvent into the formulation medium in a first step, and in a second step removing the low-boiling solvent,

D) wherein the homogeneous mixture also optionally contains one or more of inorganic or organic carrier materials, auxiliary agents and additives.

2. A method according to Claim 1, wherein one or more organoaluminum compounds are used as cocatalyst.

3. A method according to Claim 1, wherein one or more aluminoxanes are used as cocatalyst.

4. A method according to Claim 1, wherein one or more organoboron compounds are used as cocatalyst.

5. A method according to Claim 1, wherein methylaluminoxane is used as cocatalyst.

6. A method according to Claim 1, wherein one or more metallocenes of general formula (1) are used as catalyst:

$$Q(CpRa)(Cp'R'a')M(X)_n \qquad (1)$$

wherein

Cp is a cyclopentadienyl, indenyl, or fluorenyl radical,

R and R' are the same or different and each is a C_1-C_{10} alkyl, phosphine, amine, C_1-C_{10} alkyl ether, or C_6-C_{10} aryl ether group,

$0 \leq a \leq 4$ and $0 \leq a' \leq 4$,

Cp' is one of the groups Cp or

Cp' is -NR''-wherein R'' is an alkyl or aryl radical in which a is 1,

Q is a single bridge or multibridge

$$(R^1\text{-}\overset{|}{\underset{|}{Z}}\text{-}R^2)_b$$

between Cp and Cp', wherein R^1 and R^2 are the same or different and each is a hydrogen atom, a C_1-C_{10} alkyl

group, or a C_6-C_{10} aryl group, and Z denotes carbon, silicon, or germanium, in which b is 0, 1, 2, or 3,
M is a transition metal of any of the groups 3-6 of the Periodic Table (IUPAC notation),
X is halogen, and
n is the oxidation number of M, reduced by 2.

7. A method in accordance with Claim 6 wherein M is Zr or Hf, and X is Cl or Br.

8. A method in accordance with Claim 1 or 6, wherein the catalyst component is one or more metallocenes selected from the group consisting of (bis(cyclopentadienyl))zirconium dichloride, (bis(methylcyclopentadienyl))zirconium dichloride, (bis(n-propylcyclopentadienyl))zirconium dichloride, (bis(isobutylcyclopentadienyl))zirconium dichloride, (bis(cyclopentylcyclopentadienyl))zirconium dichloride, (bis(benzylcyclopentadienyl))zirconium dichloride, (bis(octadecylcyclopentadienyl))zirconium dichloride, (bis(n-butylcyclopentadienyl))titanium dichloride, (bis(n-butylcyclopentadienyl))zirconium dichloride, (bis(n-butylcyclopentadienyl))hafnium dichloride, (bis(indenyl))zirconium dichloride, (bis(indenyl))dimethylzirconium, (bis(tetrahydroindenyl))zirconium dichloride, (1,2-ethylenebis(indenyl))zirconium dichloride, (1,2-ethylenebis(indenyl))hafnium dichloride,

(1,2-ethylenebis(tetrahydroindenyl))zirconium dichloride, (dimethylsilylbis(1H-inden-1-yl))zirconium dichloride, and (dimethylsilylbis(1H-inden-1-yl))hafnium dichloride.

9. A method according to Claim 1 wherein the formulation medium is a hydrocarbon with a boiling point above 150°C and a viscosity of at least 1 Pa·sec at 25°C.

10. A homogeneous mixture produced according to the method of claim 1.

11. A homogeneous mixture consisting essentially of an optionally supported catalyst system consisting of at least one metallocene and at least one cocatalyst, and a formulation medium.

12. A homogeneous mixture according to Claim 11 wherein said formulation medium is a hydrocarbon with a boiling point above 150°C and a viscosity of at least 1 Pa·sec at 25°C.